EXAFS – Extended X-Ray Absorption Fine Structure

Lecture series:
Modern Methods in Heterogeneous Catalysis Research

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Malte Behrens, FHI-AC
behrens@fhi-berlin.mpg.de
Outline

• Basics
  – Fundamentals
  – What can we learn from an EXAFS experiment?

• How to perform an EXAFS experiment?
  – Synchroton radiation
  – Experimental setup, detection

• How extract information from am EXAFS spectrum
  – The EXAFS equation
  – Data treatment

• Examples
  – Application in heterogeneous catalysis
History

• 1895  Röntgen discovered X-rays
• 1913  De Broglie measured first absorption edge
• 1920  Fricke observed fine structure above X-ray absorption edges
• 1930  Kronig proposed a LRO theory based on crystal periodicity; then a SRO theory to explain EXAFS in the GeCl\textsubscript{4} molecule
• 1960  Van Nordstrand improved XAS instrumentation, used fingerprint ID and valence shift to characterize catalysts
• 1970  Sayers, Stern, and Lytle: Modern theory, FT of EXAFS
• 1974  Synchrotron X-radiation available at Stanford, CA
• 1994  Opening of ESRF (Grenoble); 3rd Generation Synchrotron Sources
Acronyms

• XAS  X-ray Absorption Spectroscopy
• XAFS  X-ray Absorption Fine Structure
• EXAFS  Extended X-ray Absorption Fine Structure
• XANES  X-ray Absorption Near Edge Structure
• NEXAFS  Near Edge X-ray Absorption Fine Structure
Principle

- X-ray photons from the incoming beam eject core electron beyond the ionization threshold
- The atom is in an excited state, i.e. there is a core hole. Electron ejected is called a photo-electron
- The x-ray intensity is measured before and after the sample and the X-ray absorption coefficient $\mu$ is calculated

\[ I = I_0 e^{-\mu t} \]
X-ray photon absorption

sharp absorption edges in $\mu$
characteristic core level energies

EXAFS is element-specific

L.H. Schwarz, J.B. Cohen / M. Newville
Elements for EXAFS (hard X-rays)

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T. Ressler
Fine structure

EXAFS contains information about the local environment of the absorber
Isolated atom

\[
\lambda \sim (E - E_0)^{-1/2}
\]
The origin of fine structure

\[ \lambda \sim (E - E_0)^{-1/2} \]

X-ray Absorption Fine-Structure
photo-electron
Absorbing Atom
Scattering Atom

XAFS
XANES
Energy
Absorption Probability

M. Newville
**Interference effects**

**EXAFS:** Interference phenomenon between outgoing photo-electron wave and backscattered wave
EXAFS oscillations

EXAFS spectrum comprised of a series of sine waves of different amplitude representative of the different scattering paths undertaken by the photoelectron wave.

Information about interatomic distances
Information about coordination numbers
Information about the type of neighbor atom
XAFS spectrum (Mo-K)

![XAFS spectrum graph]

1.2
1.0
0.8
0.6
0.4
0.2
0.0

Energy (E) in eV

XANES
EXAFS

Edge
Constructive
Destructive
Pre-edge
Information about local geometry

Dipole transition ($\Delta l = \pm 1$)
- $s - p$
  - K edge [1s - 3p]
  - $L_1$ edge [2s - 5p]
- $p - d$
  - $L_{II}$ edge [2p$_{1/2}$ - 5d$_{3/2}$]
  - $L_{III}$ edge [2p$_{3/2}$ - 5d$_{5/2}$]

$s \rightarrow d$ is dipole forbidden for regular octahedral site symmetry becomes partially allowed upon distortion and elimination of the center of inversion (p-d hybridization - open d shell)

Information about oxidation state

Knowledge about the oxidation state

Chemical fingerprint

Pre-edge + edge + ca. 50 eV above edge

EXAFS

Photonenergie / eV

5980 6000 6020 6040 6060 6080 6100

T. Ressler

XANES / NEXAFS:
Lectures by
A. Knop-Gericke,
K. Hermann
What do we learn from EXAFS?

• **EXAFS** gives information about the local environment (up to ca. 6 Å) around a specific type of absorber atom
  – Distance to neighboring atoms
  – Type of neighboring atoms
  – Number of neighboring atoms

• **XANES** gives information about the
  – oxidation state of the absorber
  – local geometry around the absorber
EXAFS is

• independent of long range order
  – complementary to diffraction
  – gases, liquids, amorphous and crystalline solids
  – highly dispersed phases (catalysis!)

• in general a bulk technique, but has a detection limit in the ppm range
  – Nanoparticles, diluted systems, promoters (catalysis!)

• applicable in-situ (catalysis!)
EXAFS (in-situ) experiment

Radiation:
• tunable
• penetrating
X-ray source: Synchroton

- Electrons near relativistic energies are confined to a circular orbit
- They give off energy as they are deflected
- Synchroton radiation
  - **tunable**: IR (0.1 mm) to hard X-rays (0.01 nm)
  - **high intensity**: $10^6$ x higher than lab X-ray tubes
  - high collimation
  - plane polarization
  - time structure
Synchrotron beamlines

T. Tschentscher
EXAFS at HASYLAB
Monochromators

- select energy of interest (typically from ca. 200eV before to 1 keV above the edge)
- scan through this regime
- stability

S. Bare
Double single crystal monochromator

\[
n \lambda = 2 d_{hkl} \sin(\theta)
\]

Available crystals:
- Si 111: Energy range 7 - 20 keV
- Si 311: Energy range 9 - 40 keV
- Si 511: Energy range 11 - 100 KeV
Detection: Transmission geometry

S. Bare
Ionization chambers

- Photon is absorbed by gas atom (He, N\textsubscript{2}, Ar)
- Photoelectrons emitted (ionization)
- These electron initiate more ionization
- High voltage bias across plates causes electron and ions to drift in opposite directions.
- Charges collected result in current flow which is proportional to the incident x-ray intensity
Energy-dispersive XAS (DXAFS), (ESRF, ID24), ~ s/spec

T. Ressler
Sample environment

[Diagram of a sample environment with various components labeled such as Gas Feed, Catalytic Reaction Cell, X-rays, Slit, Double Crystal Monochromator, and Gas Chromatograph.]
Catalytic in-situ cells

T. Ressler

S. Bare
Raw data treatment

- The spectrum $\mu(E)$ contains the EXAFS oscillations $\chi(E)$, which contain the structural information we are interested in.

- How to extract this information from the spectrum?

Subtraction of the “bare atom” background $\mu_0(E)$

Division by the “edge step” $\Delta \mu_0(E)$
Normalization

Cu-K

Se-K: $\mu(E)$

Se-K: $\mu(E)_{\text{norm}}$

T. Ressler
EXAFS is an interference effect that depends on the wave nature of the photoelectron. It is therefore convenient to think of EXAFS in terms of the photoelectron wavenumber, $k$, rather than x-ray energy.

$$k = \sqrt{\frac{8\pi^2 m_e}{\hbar}} (E - E_0)$$

- $m_e$: mass of electron
- $E$: Energy of incoming photon
- $E_0$: Threshold energy at absorption edge
EXAFS oscillations are extracted from $\mu(k)_{\text{norm}}$ by subtraction of the “bare atom” background $\mu_0(k)$ and normalizing

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$$
$\chi(k)$ is typically weighted be $k^2$ or $k^3$ to amplify the oscillations at high $k$.

One way to separate the sine waves (scattering paths) from one another is to perform a Fourier transform.

For the Fourier transformation it is best when the amplitudes of $c(k)$ are similar thought $\chi(k)$.
Fourier transformation

The resulting magnitude of the transform now has peaks representative of the different scattering paths of the photoelectron

→ Radial distribution function $\text{FT}(\chi(k))$
Scattering paths

Mo Metal (bcc)

FT →

1st shell
2nd shell

1st shell (2.73 Å)
2nd shell (3.14 Å)
The EXAFS equation

\[ \chi(k) = S_0^2 \sum_i N_i \frac{|f_i(k)|}{kR_i^2} e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)} \sin(2kR_i + 2\delta_i + \varphi_i) \]

- \(N_i\) is the number of scattering atoms of type \(i\)
- \(R_i\) is the distance from the central atom to the scattering atom
- \(S_0^2\) is the amplitude reduction factor (due to multielectron processes).
- \(e^{-2\sigma_i^2 k^2}\) is a term to account for the disorder in the position of the atoms.
- \(e^{-2R_i/\lambda(k)}\) is a damping factor to account for the fact that the photoelectron wave is only scattered elastically over a short distance.
- \(f_i(k)\) is the scattering amplitude at atom \(i\)
- \(\delta_i\) is the phase shift undergone by the photoelectron at the central atom
- \(\varphi_i\) is the phase shift undergone by the photoelectron when it bounces off the scattering atom

S. Bare
Fitting of EXAFS data

\[ \chi(k) = \sum_j \frac{N_j S_j^2 F_j(k)}{k R_j} \cdot e^{-2 \frac{k^2 \sigma_j^2}{\lambda}} \cdot e^{\frac{2 R_j}{\lambda}} \cdot e^{\frac{3 \sigma_j^2 k^4}{2}} \cdot \sin\left[2 k R_j + \delta_j(k) - \frac{4 \sigma_j}{k^2} \right] \]

Structural model: backscattering amplitudes and phase shifts from reference spectra or calculated *ab initio* (e.g. FEFF code) and starting parameters

Fitted parameters: Least squares fitting (e.g. WinXAS package)
EXAFS Fitting: Cu LDH

Layered double hydroxide:
\[(\text{Mg, Cu})_{1-x}(\text{OH})_2\text{Al}_x(\text{CO}_3)_{2/x} \cdot m\text{H}_2\text{O}\]

10% Cu: Is it in or between the layers?

Cu-K EXAFS fitting

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<td>0.007</td>
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*In all curve-fitting procedures the amplitude reduction factor was kept fixed at $S_0^2 = 0.85$. Estimated error of the distances: 0.03 Å.*

Cu$^{2+}$ is incorporated in the LDH layers

Cu LDH: Spectra

Experimental  Fourier filtered: first three shells  Fourier filtered: third shell
EXAFS fitting: metal ordering in aurichalite

Problem: Cu/Zn ordering in aurichalcite (a possible precursor for Cu/ZnO catalysts)

Aurichalcite: \((\text{Cu,Zn})_5(\text{CO}_3)_2(\text{OH})_6\)

XRD crystal structure:

- **Structure**: P 2\(_1\)/m, monoclinic
  - a=13.8200 Å; b=6.4190 Å
  - c=5.2900 Å; \(\beta=101.04^\circ\)
  - (40% Cu)

**Structural model**: Starting parameters for EXAFS fit

Cu/Zn ordering

Cu-K EXAFS

Zn-K EXAFS

Fig. 4. (a) 80K Cu EXAFS (solid lines) and the corresponding best fits (broken lines) of aurichalcite. BM 1964, 702 (top), BM 1983,97 (middle) and BM 1937,1355 (bottom). (b) Fourier transforms of the 80K Cu EXAFS (solid lines) and the corresponding best fits (broken lines) of aurichalcite, BM 1964,702 (top), BM 1983,97 (middle) and BM 1937,1355 (bottom).

Cu on M2 (80%) & M4
Zn on M1 & M3

EXAFS in catalysis

Sn resides on the T5 site of beta-zeolite!

S. Bare
In-situ XAFS

Partially oxidized Rh-Pt/Al₂O₃ catalyst in partial oxidation of methane

EXAFS Summary

- EXAFS oscillations $\chi(k)$ are due to interference of the photoelectron wave coming from the absorber atom and backscattered waves from the neighboring atoms, various scattering paths contribute.
- The shape of $\chi(k)$ is determined by the local environment around a specific element.
- $\chi(k)$ contains information on the neighboring atom type, the inter-atomic distances and the coordination number.
- A well developed theory is available to extract this information from experimental data by least-squares fitting (careful data reduction necessary).
- EXAFS works on all kinds of material, most elements and can be applied in-situ.
- Synchrotron radiation is required.
Literature / references


• Lecture scripts of Simon Bare (UOP), Thorsten Ressler (TU Berlin), Wolfgang Bensch (Uni Kiel)